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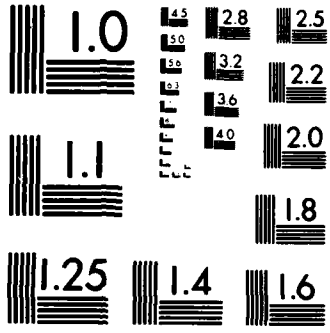

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OPTIMISATION OF THE THERMOELECTRIC FIGURE OF MERIT IN FINE GRAINED SEMICONDUCTOR MATERIALS BASED UPON LEAD TELLURIDE

INTERIM FINAL REPORT

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April 1984

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OPTIMISATION OF THE THERMOELECTRIC FIGURE OF MERIT IN FINE GRAINED SEMICONDUCTOR MATERIALS BASED UPON LEAD TELLURIDE

1. Introduction

The work relating to the optimisation of the thermoelectric figure of merit in fine grained semiconductor materials based upon lead telluride has not been completed and the programme of work is to be continued under a new contract. Consequently this report although referred to as final, actually covers progress made during the period January to March 1984. A complete final technical report will be presented on completion of the project.

2. Work undertaken

As indicated in report No 3 the next step in our investigation was the development of a theoretical model which would enable a realistic estimate to be made of the absolute magnitude of the thermoelectric figure of merit Z of materials based upon lead telluride. In report No 4 we reported the results of a preliminary investigation into the effect of including a multivallied energy band structure in our model; this was an essential step as all established thermoelectric materials, including those based upon lead telluride possess such an energy band structure. Previously workers have limited their investigation to the non-degenerate limit and we extended the analysis to cover the range of doping level encountered in practical thermoelectric materials. In addition to possessing a multivallied energy band structure, materials based upon lead telluride have narrow energy band gaps. Narrow gap semiconductors in general possess non-parabolic energy surfaces and the difficulties encountered in obtaining a satisfactory agreement between theory and experimental data has been resolved by including non-parabolicity in our theoretical model.

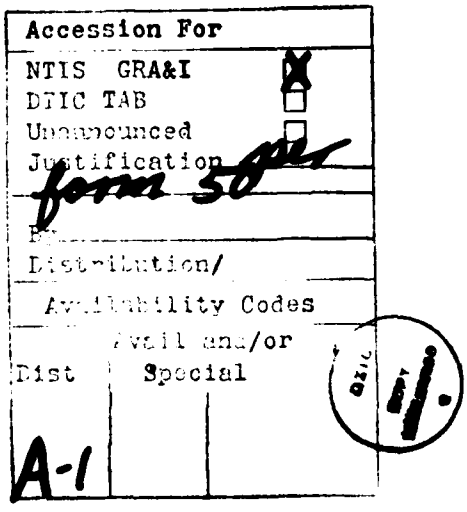
The results of our analysis of the Lorenz factor and the electronic thermal conductivity indicates that meaningful information on the thermoelectric behaviour of narrow band gap semiconductors can only be derived from a model which takes into account the following factors: (a) Multivallied energy band structure; (b) Non-parabolic energy bands; (c) Minority carrier effects at relatively high temperatures. The results of this phase of the work are embodied in

the two papers entitled "Thermoelectric behaviour of a multi-vallied semiconductor" and "Electronic thermal transport in thermoelectric material - effect of nonparabolicity" which were presented at the Fifth International Conference on Thermoelectric Energy Conversion, Arlington, Texas, March 14-16, 1984.

Parallel to the theoretical investigation an attempt will be made to prepare materials based upon lead telluride with improved thermoelectric figures of merit. Samples of n- and p-type materials have been provided by "Global thermoelectrics", Alberta, Canada. A quantity of <5 μm particle size material has been prepared and the vacuum hot press is being brought into commission.

3. Future Programme of Work

As indicated previously the work will continue under a new contract. The next stage of the theoretical investigation will be to obtain the variation of the absolute value of Z with carrier concentration and temperature; including all three factors (a), (b) and (c) cited above in the theoretical model. Practical work will centre around commissioning the vacuum hot press.



(Proceedings of the 5th International Conference on Thermoelectric Energy Conversion
Arlington, Texas - March 1984 Paper II-2)

THERMOELECTRIC BEHAVIOUR OF A MULTIVALLIED SEMICONDUCTOR

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ABSTRACT

Following the usual procedure for including the effects of a multivallied energy band structure, the ratio $(ZT)_{mv}/(ZT)_{sv}$ has been obtained as a function of reduced Fermi energy (ξ), where $(ZT)_{mv}$ and $(ZT)_{sv}$ refer to the dimensionless thermoelectric figure of merit of a multivallied and single vallied semiconductor respectively, both with and without intervalley scattering. The results obtained agree with those previously reported in the limit of non degeneracy but the effectiveness of a multivallied structure in improving the figure of merit is reduced with increasing ξ. It is concluded that at ξ_{opt} it is still an advantage to use a multivallied semiconductor while the inclusion of intervalley scattering may decrease $(ZT)_{mv}/(ZT)_{sv}$ by about 25-30 percent.

1. INTRODUCTION

It has been recognized for some considerable time that a multivallied semiconductor (mv) is more suitable for thermoelectric application to one which has a single valley (sv). Of the large number of semiconductors which have been examined, bismuth telluride, lead telluride (and their alloys) and silicon germanium alloys are established as the best thermoelectric materials over their respective temperature ranges of operation [1]. All these materials possess a multivalley energy band structure.

In the non-degenerate limit the thermoelectric figure of merit (ZT) has been shown to increase linearly with the number of valleys, if intervalley scattering is neglected [2,3]. However in practice thermoelectric materials are doped to relatively high carrier concentrations in order to optimise the figure of merit. A multivalley energy band structure and intervalley scattering may have a significantly different effect on Z in the region of optimum doping compared to that in the non-degenerate limit [4]. In this paper we examine the effect of a multivalley energy band structure and intervalley scattering on the thermoelectric figure of merit as a function of carrier concentration (expressed in terms of reduced Fermi energy ξ).

A rigorous calculation of the effect of intervalley scattering is difficult. Herring [5], however has developed a theoretical framework, which includes intervalley scattering, to obtain the temperature dependence of mobility. For a single valley i, a conductivity tensor $\sigma^{(i)}_{\alpha\beta}$ and a mobility tensor $\mu^{(i)}_{\alpha\beta}$ can be defined. The total conductivity tensor $\sigma^{\alpha\beta}$ due to the carriers in all the valleys in a multivalley energy band is given by $\Sigma\sigma^{(i)}_{\alpha\beta}$ whereas the overall mobility tensor is the average of $\mu^{(i)}_{\alpha\beta}$ over different valleys. The temperature dependence of the mobility has been obtained by Herring in terms of a ratio W_2/W_1, where W_2 and W_1 are measures of the coupling of carriers via intervalley and intravalley modes. For example:- when intervalley scattering is absent $W_2/W_1 = 0$. In the present investigation the value of W_2/W_1 has been chosen to provide the correct order of carrier mobility.

Acoustic phonon scattering has been taken as the dominant scattering mechanism. Polar optical scattering is not insignificant in PbTe and its role will be discussed in detail in a future communication. The author has discussed in detail the thermoelectric properties of semiconductor models which possess single ellipsoidal energy surfaces, single ellipsoidal energy surfaces, multivalley energy surfaces. In his analysis he considered non-degenerage extrinsic material and assumed that the reduced Fermi energy can be varied independently of the scattering parameter(s).

2. THEORETICAL MODEL

a. Non-degenerate limit

The figure of merit at optimum doping is usually expressed as a function of a parameter A:-

$$\text{where } A \propto T\left(\frac{\mu_c}{\lambda_L}\right)\left(\frac{m^N}{m_0}\right)^{3/2} \qquad (1)$$

$$\text{and } m^N = N_v^{2/3}(m_1^* m_2^* m_3^*)^{1/3} \qquad (2)$$

m_1^*, m_2^* and m_3^* are the components of the effective mass tensor along principal directions. Assuming that the relaxation time depends on carrier energy as E^s, the density of states effective mass for one valley in the multivalley case is the same as that for a single valley, ie. $m^* = (m_1^* m_2^* m_3^*)^{1/3}$, and neglecting any intervalley scattering, it can be shown that

$$\frac{A_{mv}}{A_{sv}} = \frac{(\lambda_L)_{sv}}{(\lambda_L)_{mv}} \frac{N_v(1+2a)}{3a^{2/3}} \qquad (3)$$

Here $m_2 = m_3$ and $m_1 = am_2$

Evidently the figure of merit increases with the number of valleys N_v.

b. Higher doping levels

Of interest is the effect of a multivalley band structure on the figure of merit of materials which have been optimally doped ($\xi = 0$).

For a single band conduction model and a single spherical valley, the dimensionless figure of merit is given by

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$$(ZT)_{sv} = \frac{(\mathcal{L}_e)^2 \sigma'_{e_{sv}}}{1+\sigma'_e (\mathcal{L}_e)_{sv}} \qquad 4$$

Where $\mathcal{L}_e$ is the Lorenz factor and σ' and α' are the reduced electrical conductivity and Seebeck coefficient respectively [1,6]. A multivalley energy band is incorporated in the model through its effect on the electrical conductivity. As ξ is taken as an independent parameter α'_e is uneffected by the number of valleys. The same is true in our model of the effect of intervalley scattering.

The effect of incorporating a multivallied structure can be conveniently discussed by a plot of the ratio

$$\frac{(ZT)_{mv}}{(ZT)_{sv}} = \frac{\sigma'_{e_{mv}}}{\sigma'_{e_{sv}}} \cdot \frac{1+\sigma'_e (\mathcal{L}_e)_{sv}}{1+\sigma'_e (\mathcal{L}_e)_{mv}} \qquad 5$$

Evidently in the non-degenerate limit

$$\sigma'_e (\mathcal{L}_e) \ll 1 \qquad 6$$

and since

$$\sigma'_{e_{mv}} = N_v \sigma'_{e_{sv}} \qquad 7$$

$$\frac{(ZT)_{mv}}{(ZT)_{sv}} \to N_v \quad (-\xi \gg 1) \qquad 8$$

3. RESULTS AND DISCUSSIONS

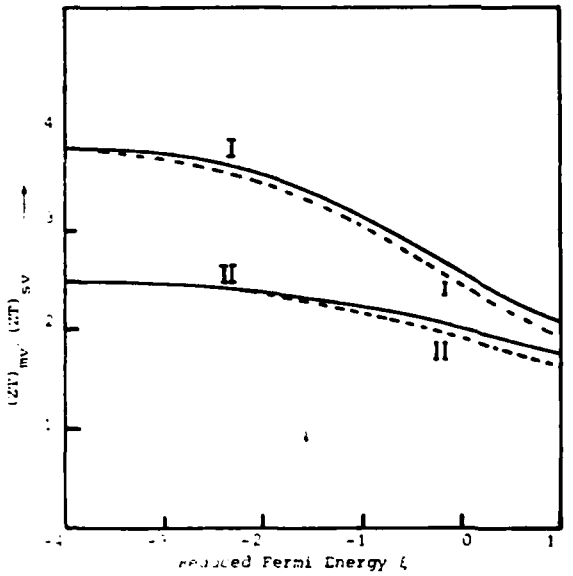

Figure 1. $(ZT)_{mv}/(ZT)_{sv}$ plotted against ξ for PbTe at 300 K. Parabolic bands — Acoustic scattering ---- Polar optical scattering (I) without I.V.S. (II) with I.V.S., $W_2/W_1=0.5$, single band model.

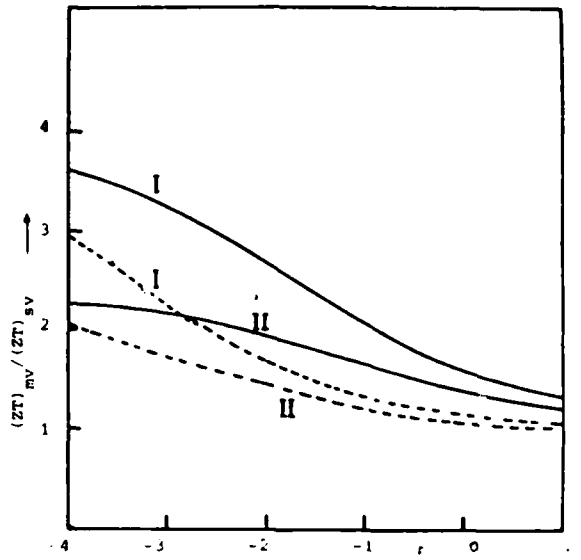

Figure 2. $(ZT)_{mv}/(ZT)_{sv}$ plotted against ξ for PbTe at 300 K. — Acoustic scattering, ---- Polar optical scattering, (I) without I.V.S. (II) with I.V.S., $W_2/W_1=0.5$.

Although the analysis presented is a general one we have chosen parameters which correspond to lead telluride. Figures 1 and 2 display the results of our calculations. At $\xi=-4$, $(ZT)_{mv}/(ZT)_{sv}$ is close to $N_v(=4$ without the inclusion of intervalley scattering; including intervalley scattering ($W_2/W_1=0.5$) reduces it to about 2.5 at 300K.

Within the framework of the model adopted the following conclusions can be drawn from the results of our calculations.

a. In the non-degenerate limit the ratio $(ZT)_{mv}/(ZT)_{sv}$ acquires its highest value and as ξ increases it approaches a value of unity in the degenerate limit.

b. The inclusion of intervalley scattering lowers the ratio considerably in the non-degenerate limit while in the degenerate limit the ratio $(ZT)_{mv}/(ZT)_{sv}$ with and without the inclusion of intervalley scattering are almost identical.

c. In the region of optimum doping ($-1<\xi<0$), the intervalley scattering reduces the ratio $(ZT)_{mv}/(ZT)_{sv}$ by approximately 25-30 percent. However evidently it is still advantageous to employ thermoelectric materials which possess a multivalley energy band structure.

ACKNOWLEDGMENTS

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(Proceedings of the 5th International Conference on Thermoelectric Energy Conversion
Arlington, Texas - March 1984 Paper VI-3)

ELECTRONIC THERMAL TRANSPORT IN THERMOELECTRIC MATERIAL - EFFECT OF BAND NON-PARABOLICITY

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ABSTRACT

In this paper the effect of non-parabolic energy bands and minority carriers on the electronic thermal conductivity κ_e and the thermoelectric figure of merit Z of narrow band gap semiconductors is investigated. The analysis indicates that if non-parabolicity is not taken into account, the theoretical values obtained for κ_e and Z considerably overestimate those observed experimentally in PbTe and Bi_2Te_3. Minority carrier effects, although relatively unimportant in PbTe at around room temperature are significant in Bi_2Te_3 and consequently a two band model must be employed.

1. INTRODUCTION

In general, semiconductors with high thermoelectric figures of merit possess a multivalley energy band and a narrow energy gap. Although the latter requirement is a contributory factor in limiting the upper operating temperature, narrow gap materials such as those based upon bismuth telluride and lead telluride are widely employed in thermoelectric applications. Minority carrier effects may be significant in narrow gap semiconductors at relatively low temperatures consequently a "two band model' should be employed in an analysis of their thermoelectric transport properties. In addition narrow gap semiconductors have been shown to possess a significant degree of band non-parabolicity and the transport behaviour of InSb [1] and the lead chalcogenides [2] have been discussed in the literature.

In this paper we examine the effect of band non-parabolicity and minority carriers on the electronic thermal conductivity and thermoelectric figure of merit of materials based upon bismuth telluride and lead telluride.

2. THEORETICAL FRAMEWORK

A two band model is considered with the carrier effective mass (m*) depending on energy ε as:-

$$m^* = m_c^*(1+2\varepsilon/\varepsilon_g) \qquad 1$$

m_c^* refers to the value of m* at the band edge and ε_g is the energy gap.

The density of states effective mass is given by:-

$$m_d^* = N_v^{2/3}(m_{||}^* m_{\perp}^{*2})^{1/3} \qquad 2$$

N_v is the number of equivalent valleys with $m_{||}$ and $m_{\perp}$ the longitudinal and transverse components of the effective mass tensor.

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The dimensionless figure of merit for a two band model can be written as

$$ZT = \frac{(\alpha_h'\sigma_h' - \alpha_e'\sigma_e')^2}{(\sigma_e'+\sigma_h')\ (1+\sigma_e'\mathcal{L}_e+\sigma_h'\mathcal{L}_h)+\sigma_e'\sigma_h'(\delta_e+\delta_h+\xi_g)^2}$$

Suffices e and h refer to contributions from electrons and holes and the α' and σ' are dimensionless quantities as described in references [3,4]. The single band case can readily be discussed by taking $\sigma_h'=0$.

3. NON-PARABOLIC ENERGY BANDS

The parameters which occur in equation (3) and in the case of a parabolic band as described in refs [3,4] are modified for a non-parabolic band [2,5]. The transport equations can be written in terms of the generalized Fermi integrals defined by

$${}^{n}L_{\ell}^{m} = \int_0^{\infty} \left(-\frac{\partial f}{\partial \eta}\right) \eta^n [\eta(1+\beta\eta)]^m (1+2\beta\eta)^{\ell} d\eta \qquad 4$$

Here $\eta = (\varepsilon/kT)$ is the reduced carrier energy, $\beta = \frac{kT}{\varepsilon_g}$ is the inverse of the reduced energy band gap and f is the usual Fermi function. For acoustic scattering of carriers the Lorenz factor is expressed as

$$\mathcal{L} = ({}^{2}L_{-2}^{1}/{}^{0}L_{-2}^{1}) - \delta^2 \qquad 5$$

$$\text{where } \delta = {}^{1}L_{-2}^{1}/{}^{0}L_{-2}^{1} \qquad 6$$

The reduced electrical conductivity is given by

$$\sigma' = KN_v\,{}^{0}L_{-2}^{1}T/(m_c^*\lambda_L) \qquad 7$$

$$\text{where } K = \frac{k_B^2 hC_{||}}{3\pi^2\varepsilon_1^2} \qquad 8$$

$C_{||}$ and ε_1 refer to the longitudinal elastic constant and deformation potential respectively.

The reduced Seebeck coefficient is given by

$$\alpha' = \pm\,(\delta(\xi)-\xi)$$

with $\delta(\xi)$ for the non-parabolic case is given by Equation (6).

4. RESULTS

The room temperature variation of the Lorenz factor and of the ratio of the electronic to lattice thermal conductivity (λ_e/λ_L) with reduced Fermi energy (ξ) are plotted in figures 1 and 2 for PbTe and Bi_2Te_3 respectively. It is apparent that the value of $\mathcal{L}$ and of λ_e/λ_L are reduced when non-parabolicity of the energy bands is taken into consideration. In thermoelectric applications the doping levels which correspond to a maximum in ZT are of particular interest and the values of various parameters given in Table 1 correspond to ξ_{opt}.

The influence of minority carriers on the figure of merit is conveniently demonstrated by plotting the factor $\left[(ZT)_{SB}-ZT\right]/ZT$ against ξ at different temperatures. $(ZT)_{SB}$ and ZT refer to single band and two band models respectively. The results for PbTe and Bi_2Te_3 are shown in figures 3 and 4.

It is concluded that the inclusion of non-parabolic energy bands significantly affects the thermoelectric transport coefficients and consequently the figure of merit. The inclusion of non-parabolicity results in better agreement between the theoretical and experimental values of λ_e/λ_L and ZT. A two band model must be employed for Bi_2Te_3 even at room temperature and for PbTe at temperatures above about 700K.

TABLE 1

Lorenz factor $\mathcal{L}$, λ_e/λ_L and ZT at ξ_{opt} (room temperature)

	ξ_{opt}	$\mathcal{L}$ (par.)	$\mathcal{L}$ (nonpar.)	λ_e/λ_L (par)	λ_e/λ_L (nonpar)	ZT (par)	ZT (nonpar)	λ_e/λ_L (exp)	ZT (exp)
PbTe	~-0.75	2.1(3.0)	1.66(2.7)	0.42(0.8)	0.24(0.5)	1.3	~0.56	0.15	0.9
Bi_2Te_3	~-0.65	2.1	1.5	0.55	0.21	0.92	~0.56	0.25	~0.6

The intervalley scattering included in the calculations with $w_2/w_1=0.5$, w_2 and w_1 refer to the strength of coupling of carriers to intervalley and intravalley modes [8]; bracketed quantities in the case of PbTe refer to values of the various parameters appropriate to the polar optical scattering (based on preliminary calculations)

Acoustic phonon scattering is assumed to be the sole scattering mechanism operative at 300K. Although this assumption is correct for Bi_2Te_3 optical phonon scattering is not insignificant in PbTe and must be included in a rigorous analysis. Detailed calculations of the polar optical contribution are in progress and the results will be communicated at a future date. The results of preliminary investigations are included in Table 1 (bracketed quantities). Experimentally determined values of λ_e/λ_L are given for comparison.

A rigorous quantitative estimate of the various thermoelectric transport coefficients would require an accurate estimate of intervalley scattering and of the temperature variation of effective mass. Although the present analysis is a semiquantitative one the results obtained are relatively insensitive to moderate changes in these parameters.

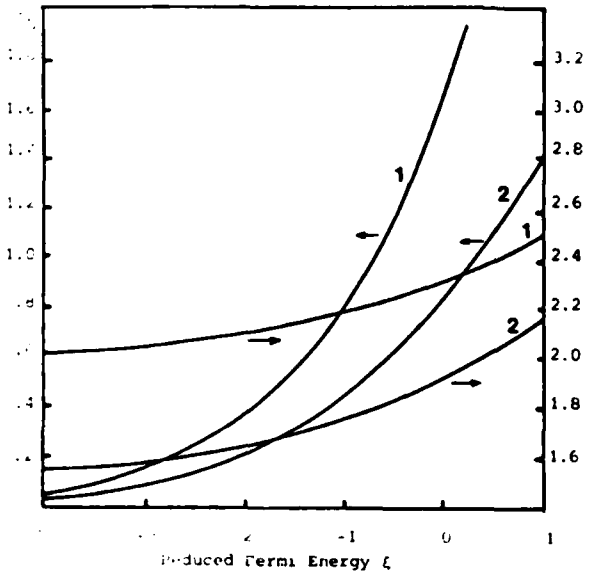

Figure 3. The quantity λ_e/λ_L or $\mathcal{L}_{e,e}$ plotted against ξ for PbTe at 300K. Acoustic scattering, $w_2/w_1 = 0.5$. 1. Parabolic 2. Non parabolic.

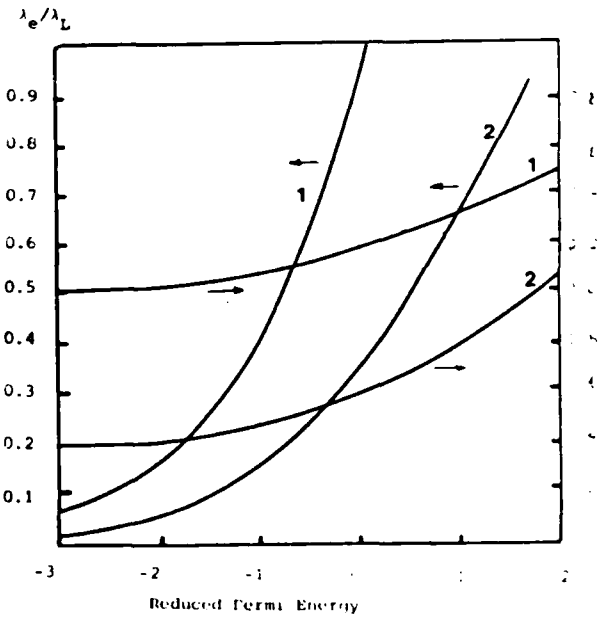

Figure 2. The quantity λ_e/λ_L or $\mathcal{L}_{e,e}$ plotted against ξ for Bi_2Te_3 at 300K. Acoustic scattering, $w_2/w_1 = 0.5$. 1. Parabolic, 2. Non parabolic.

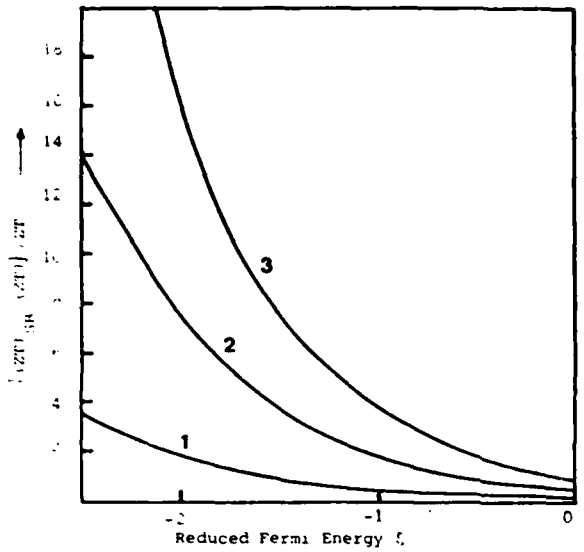

Figure 3. The ratio $\left[(ZT)_{SB}-(ZT)\right]/ZT$ plotted against ξ for PbTe at different temperatures. 1.500K 2.700K 3.900K.

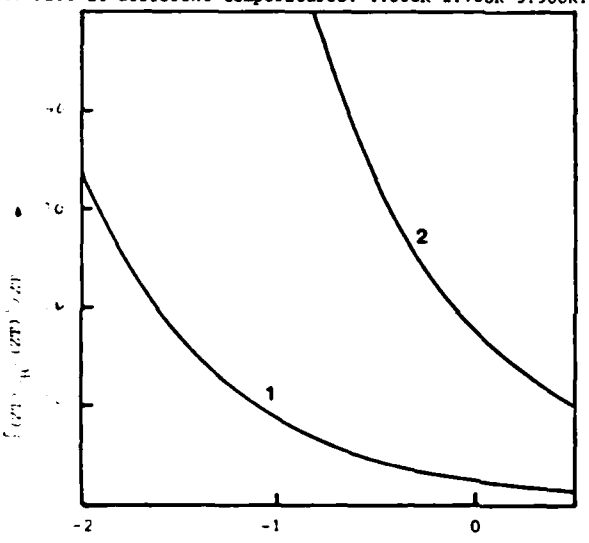

Figure 4. The ratio $\left[(ZT)_{SB}-(ZT)\right]/ZT$ plotted against ξ for Bi_2Te_3 at different temperatures. 1. 300K 2. 500K.

ACKNOWLEDGEMENTS

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